Electrochemical characterization of undoped hydrogen terminated diamond

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Hydrogen terminated diamond shows two properties which attract significant attention and controversial discussions. The first property is the negative electron affinity (NEA) of about -1.1 to -1.3 eV which is generated by C-H dipoles at the surface [1]. The second property which can be detected in combination with H-termination is a conductive p-type surface layer, detectable on samples which are exposed to air. It is assumed that the conductive layer is generated by transfer doping where valence-band electrons diffuse into a wetting layer of appropriate pH value. Contrary to this proposal, the pH-sensitivity of such layers has been reported not to follow this prediction [2].

In this paper we discuss cyclic voltammetric experiments performed for the first time on several undoped H-terminated single crystalline diamond films, using different redox couples in electrolytes in a triode chemical reactor where the working electrode is diamond, the counter electrode is Pt and the reference electrode is saturated Calomel. The diamond substrates (Ib and IIa) have been homoepitaxially overgrown and hydrogen terminated at 800 ^{o}C in H_2 atmosphere (25 Torr) using a microwave plasma discharge (750 W). After cooling of the sample to RT, a mechanical cleaning has been applied to remove a soft carbon layer, which forms during the cooling in the plasma/H_2 atmosphere.

We applied cyclic voltammetric experiments as the chemical potentials of the electrolytes are known and can be varied by change of the redox couple/electrolyte system. The results (a typical example is shown in Fig. 1 for Ferrocyanide in Na_2SO_4) reveal: a) Undoped hydrogen terminated diamond is a perfect electrode with a chemical window in the range -2.4 V to +1.5 V. b) For voltages larger than +1.5 V oxidation takes place which can be monitored by detection of the peak currents. c) For Ferrocyanide, the peak currents are separated by about 625 mV which is a result of the electron transfer rate limiting diamond electrode. We apply the Marcus-Gerischer Model [3] to discuss these features. In addition, we have realized pH-detectors based on H-terminated diamond to measure the pH-dependence of the surface conductive channel in different electrolytes and find that the surface conductivity follows the Nernst equation nearly perfectly (56 mV/pH). The channel current of typical 10 μA is confined in a narrow energy well which shows leakage currents in the range of nano-amperes. The hole-density is photosensitive to light of 4 to 4.5 eV as detected by photocurrent experiments. In addition, for these

photon energies we also detect an onset of secondary photoelectron emission by total photoyield experiments which may be important to understand the photochemical attachment of amine groups on diamond.

Our experiments clearly reveal that a perfectly hydrogen terminated and clean diamond surface has an unpinned surface Fermi level, which gives rise to surface conductivity by transfer doping according to the Nernst equation. Our results will be discussed in detail taking into account the chemical potentials, the NEA and the specific properties of cyclic voltammetry experiments.

1) F. Maier, J. Ristein, L. Ley, Phys. Rev. B 64, 165411 (2001).

2) H. Kawarada, Y. Araki, T. Ogawa,, H. Umezawa, pys. stat. sol. A, 185, 79 (2001).

3) H. Gerischer, in „Physical Chemistry: An Advanced Treatise", Vol. 9A, H. Eyring, D. Henderson, W. Jost, Eds., Academic, New York, 1970.

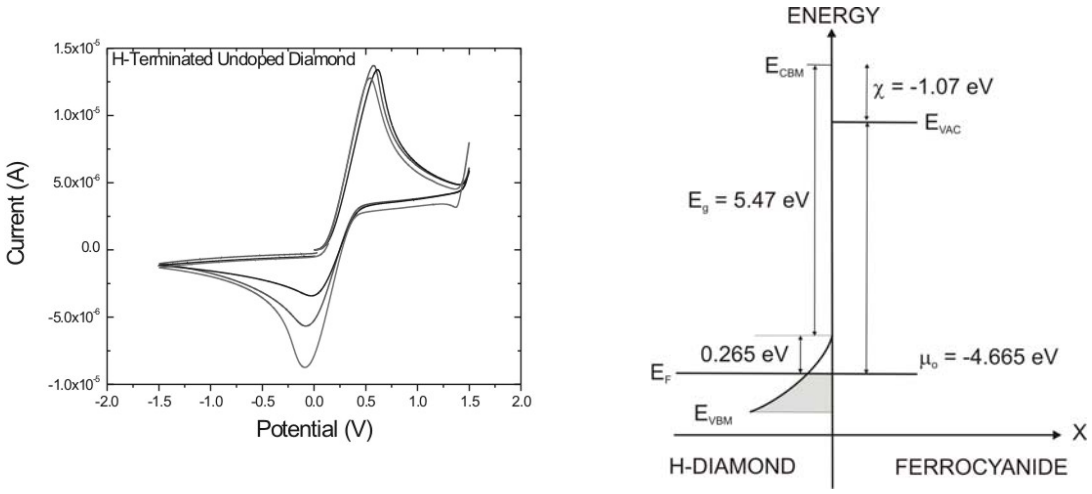

Fig. 1: Typical cyclic voltagrams, using Ferrocyanide in Na_2SO_4 and H-terminated diamond and the related energy diagram of the diamond/electrolyte-redox system.

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